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Simultaneous measurements of CO_2, CH_4, and N_2O in air extracted by sublimation from Antarctica ice cores: Confirmation of the data obtained using other extraction techniques

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Abstract. A sublimation technique has been developed to extract air samples from polar ice cores for subsequent simultaneous measurement of several trace gases by frequency-modulated tunable diode laser absorption spectroscopy. This extraction and analysis technique is shown to be suitable as an extraction method for the determination of concentrations of the greenhouse gases CO_2, CH_4, and N_2O in air samples of ~1–5 cm^3 recovered from ice samples of 10–50 g. Air samples from the Siple ice core have been analyzed covering the period between 1772 and 1973. In addition, a few samples from two different ice cores from Vostok station have been analyzed. Our results are in a good agreement with results obtained by other researchers using melting and crushing extraction techniques. This agreement indicates that processes connected with the formation of clathrates in ice under high pressure at greater depths and their destruction after drilling are not affecting the CO_2, CH_4, and N_2O measurements significantly.

1. Introduction

The composition of the ancient atmosphere and its global change during the past 220 kyr can be reconstructed most directly from the analysis of air bubbles entrapped in polar ice cores [*Oeschger and Langway*, 1989; *Jouzel et al.*, 1993; *Raynaud et al.*, 1993]. So far, a change of mixing ratios of CO_2, CH_4, and N_2O has been reconstructed from different ice cores [e.g., *Neftel et al.*, 1985; *Barnola et al.*, 1987; *Zardini et al.*, 1989; *Chappellaz et al.*, 1990; *Barnola et al.*, 1991; *Staffelbach et al.*, 1991; *Jouzel et al.*, 1993; *Chappellaz et al.*, 1993; *Raynaud et al.*, 1993], and its relationship with the changing climate or with anthropogenic activities has been investigated. Only recently, a change of CO mixing ratios during the last 200 years has been reported as well [*Haan et al.*, 1996].

The basis for these investigations is the assumption that the composition of the air extracted from ice core samples represents the air composition at the time of the closure of the bubbles. This assumption implies that physisorption and chemisorption of air components at firn grain surfaces and fractionation effects due to gravity separation and thermodiffusion in the firn can be neglected or corrected for and that the composition of air after enclosure in bubbles is not altered by chemical reactions between impurities in the ice. A good agreement of trace gas measurements in air samples from firn and ice overlaping in time with direct measurements in the atmosphere [*Neftel et al.*, 1985; *Etheridge et al.*, 1992; *Raynaud et al.*, 1993; *Battle et al.*, 1996] shows that physisorption and chemisorption do not influence the composition of the air bubbles at least on the decadal timescale and for gases measured so far. The presence of chemical reactions has been documented by a detailed intercomparison of CO_2 measurements in ice cores from Greenland and Antarctica [*Anklin et al.*, 1995] which has shown excess CO_2 built up in Greenland ice cores either by oxidation of organic carbon, the reaction between ice acidity and carbonate, or both. In great depth under high hydrostatic pressure, air gets enclosed into clathrates. Fractionation of gases could occur if the extraction yield of the air sampling is below 100% [*Schwander*, 1989; *Anklin et al.*, 1997] as it is in the case with extraction techniques using mechanical crushing of the ice samples. The consistency of trace gas measurements on different ice cores at sites with different snow accumulation rates and therefore exposed to different pressures [e.g., *Barnola et al.*, 1987; *Chappellaz et al.*, 1990; *Leuenberger and Siegenthaler*, 1992; *Raynaud et al.*, 1993] provides an indirect indication that clathrate formation and decomposition do not cause serious fractionation of the air composition. However, a direct confirmation that the air composition is not significantly affected by these processes is still missing.

In a recent paper, *Güllük et al.* [1997] reported on the development of a nondestructive technique for simultaneous determination of CO_2, CH_4, N_2O, and CO in air samples of a few cubic centimeters. The technique is based on a frequency-modulated high-resolution infrared absorption spectrometer with tunable diode lasers (FM-TDLAS) and is capable of measuring ambient mixing ratios of CO_2, CH_4, and N_2O in 2 cm^3 of air with a precision of 1%–2%. The technique has been developed for the analysis of air samples extracted from 20–50 g ice core samples. A simultaneous determination of three or four target gases in an ice sample of this size represents a significant improvement in comparison with the current ana-

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lytical techniques which require substantially larger ice samples for the same performance in most of the laboratories [e.g., *Etheridge et al.*, 1988; *Machida et al.*, 1995]. However, to utilize the potential of this analytical technique, an extraction technique suitable for all the target gases has to be used. Because of possible CO_2 artefacts, extraction by melting of ice [e.g., *Chappellaz et al.*, 1990; *Haan et al.*, 1996] is not suitable for this purpose [*Delmas*, 1993]. Mechanical crushing or milling of ice samples [e.g., *Zumbrunn et al.*, 1982; *Barnola et al.*, 1987; *Etheridge et al.*, 1988] in devices made of metal produced CH_4 contamination from the grinding of metal and special designs were needed to reduce this contamination to acceptable levels [*Fuchs et al.*, 1991]. However, smaller or larger fragments of ice are still intact after crushing and can thus contain undestructed clathrates. The extraction efficiency by crushing ice with clathrates is only 45%–70% efficient [*Anklin et al.*, 1997], so that fractionation is possible. For these reasons we concentrated on the development of the sublimation extraction technique.

Wilson and Donahue [1990] and *Wilson* [1995] recently reported the use of sublimation of the ice as a technique for the extraction of air samples from ice cores. They applied this technique to extract air samples for the determination of the isotopic composition of CO_2 in ice cores. Their measurements of preindustrial CO_2 mixing ratios, however, suggest that substantial amounts of CO_2 and possibly of other trace gases may be contained in the ice matrix, inaccessible to crushing extraction techniques [*Wilson*, 1995]. The comparison of air sample extraction by sublimation developed by us with other extraction techniques can contribute to a resolution of the questions raised by Wilson [e.g., *Powell*, 1994].

In this paper we report on the development of the sublimation extraction technique and a few measurements on ice core samples to demonstrate its viability. The sublimation extraction technique has been developed (1) to complement the FM-TDLAS technique, (2) to solve the problem of a possible fractionation of gases from ice where air is enclosed in clathrates (because of the incomplete extraction with the crushing techniques), and (3) to allow new measurements (e.g., gas composition of air occluded in firn grains). The reliability of the sublimation extraction technique was demonstrated by measurements on the Siple ice core. The results of these measurements were in a good agreement with measurements made by other researchers using melting and crushing extraction techniques. The good agreement of the results from the Vostok ice core obtained by sublimation with those obtained by other techniques indicates that processes connected with the disappearance of air bubbles in ice under high pressure at greater depths and their reappearance after drilling do not lead to a significant fractionation of the measured trace gases. The agreement of our measurements on Siple and Vostok ice cores with measurements by *Neftel et al.* [1985], *Stauffer et al.* [1985], *Barnola et al.* [1987], *Blunier* [1992], *Jouzel et al.* [1993], and *Machida et al.* [1995] shows that the sublimation extraction technique is suitable for simultaneous CO_2, CH_4, and N_2O measurements in ice cores. CO measurement has also been attempted but so far has failed because contaminations were too high.

2. Experimental Section

Measurements of trace gases in air extracted from ice samples are made in three steps: (1) extraction of the air sample from the ice core sample, (2) transfer of the extracted air from the extraction apparatus into the absorption cell of the spectrometer, and (3) determination of the trace concentrations by a frequency-modulated tunable diode laser (FM-TDLAS) absorption spectrometer.

2.1. Apparatus for Ice Sublimation

The sublimation extraction technique utilizes sublimation of the ice sample in a high-vacuum apparatus at temperatures well below the triple point of ice-water-vapor (0°C). The energy needed for the sublimation is transferred to the ice sample by near infrared irradiation. The released water vapor and the air from the bubbles are refrozen in consecutive cold traps at temperatures appropriate to separate both components. The temperature of the ice during sublimation is monitored via the water vapor pressure above the ice and kept below −20°C (equivalent to 1 hPa vapor pressure) to prevent melting and the formation of the quasi-liquid layer on the ice surface reported by *Elbaum et al.* [1993] and *Furukawa et al.* [1987] at temperatures between −4° and −2°C and at the interface between the ice and glass [*Furukawa et al.*, 1993]. These measures should prevent chemical reactions in the liquid phase from producing excess CO_2 from carbonate dust.

The sublimation apparatus is shown schematically in Figure 1. The essential parts of the apparatus are the sample vessel A in which the ice sample is placed and the ice vapor trap B for freezing out the bulk of the water vapor. Air released during the sublimation flows through the thin tubing reaching the bottom of the ice vapor trap B via a second ice vapor trap C to a cold finger where it is condensed at 14 K. The apparatus was installed in a laboratory at ambient temperature.

With the exception of the cold finger made of stainless steel the apparatus is made almost completely of glass (Duran). Except for the valve of the calibration gas cylinder, only high-vacuum glass stopcocks with teflon o-rings (Fa. Young) are used in that part of the apparatus where the sublimation takes place and where the water vapor pressure is relatively high. We preferred these materials to stainless steel because a former apparatus built up of ultrahigh-vacuum stainless steel components introduced higher levels of contamination.

Both traps B and C are kept at −90°C using a closed cycle alcohol cryocooler (HAAKE KT 90). The cold finger is cooled down to 14 K by a two-stage closed cycle He cryocooler of Gifford-McMahon type (RGD 210, Leybold). The whole sublimation apparatus is evacuated by a turbomolecular pump combined with a rotary vane pump as a forepump. The pressure is monitored by two pressure gauges: an ionization vacuum gauge covering a pressure range between 10^{-9} and 10^{-2} hPa during the evacuation of the apparatus and a capacitance pressure gauge (Leybold CM 10, 1×10^{-3} − 13 hPa) for the continuous monitoring of the vapor pressure during sublimation. The temperature of the ice sample is not measured directly but inferred from the measurements of the pressure in the sublimation apparatus.

To sustain a high sublimation rate, a sufficient amount of energy has to be transferred to the ice sample. This has been achieved by irradiation of the ice sample by four near IR quartz lamps whose total power can be adjusted between 0 and 1200 W using a variable autotransformer. To prevent overheating of the walls of the sample vessel by partially absorbed IR energy and heat from the surrounding air and, consequently, a local melting of the ice sample, the annulus between the lamps and the ice sample vessel is flushed by an intensive stream of air cooled down by liquid nitrogen.

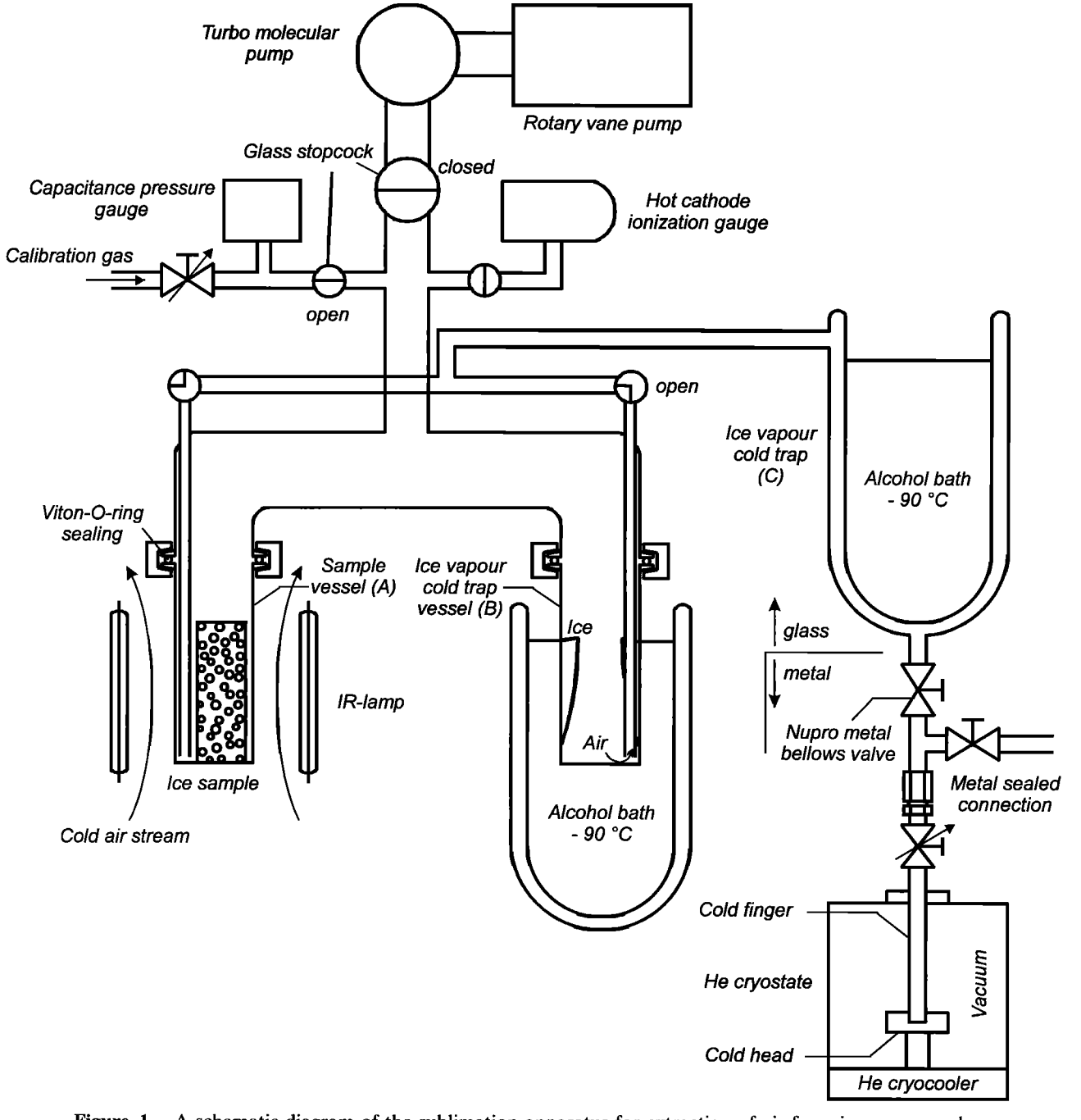

Figure 1. A schematic diagram of the sublimation apparatus for extraction of air from ice core samples.

2.2. Sublimation Procedure

A cube of ice sample weighing 20–50 g is cut with a band saw from the ice core in a cold room at −24°C and placed into sample vessel A. The vessel with the sample is attached to the apparatus, and the apparatus is evacuated. During the evacuation, ambient air in the vessel is pumped off, and a thin layer of the surface of the ice sample with adsorbed gases is evaporated and pumped off as well. This is an important cleaning process. The IR quartz lamps are switched off during this evacuation so that the ice sample is cooled down well below −24°C because of the loss of sublimation heat.

After evacuation for at least 2 hours the pump is shut off, both cold traps B and C are cooled down to an operating temperature of −90°C, and the ice sample is irradiated by the infrared lamps. The ice sublimes, and because of the large cross section of tubing between vessels A and B in comparison with the small cross section of tubing leading to the trap C, the ice vapor is almost completely trapped in cold trap B. The total pressure consisting of the partial pressures of both the ice vapor and the released air is monitored. The partial pressure of air is smaller than that of the ice vapor by ~5 orders of magnitude. The intensity of the irradiation is controlled to keep the ice vapor pressure within 0.2–0.5 hPa (corresponding to ice temperatures of −36°–−27°C) during sublimation, thus preventing the formation of a quasi-liquid layer on the ice surface. Keeping the ice vapor pressure at low levels also re-

duces substantially the desorption of CO_2 molecules adsorbed at the system's inner walls by water molecules as reported by *Zumbrunn et al.* [1982].

Air released in the course of the sublimation procedure is carried by the continuous flow of ice vapor to trap B and then flows through the thin pipe into cold trap C where the rest of the ice vapor is frozen out. The remaining partial pressure of ice vapor after passing this trap amounts to 1×10^{-4} hPa (corresponding to −90°C). The almost dry air is then condensed in the cold finger (stainless steel tube, 166 mm long, ID 14 mm, wall thickness 1 mm) at 14 K. Sublimation of 50 g of natural ice takes 30–45 min and is strongly dependent on its surface area exposed to the irradiation. In the initial part of the sublimation process, when there is an inhomogeneous temperature distribution within the ice sample, it may break in two or more pieces which substantially accelerates the sublimation process.

2.3. Transfer of the Extracted Air Into the Absorption Cell of the Spectrometer

After completing the sublimation procedure the valve on the cold finger is shut. The closed cold finger is then disassembled from the sublimation apparatus and warmed up to ambient temperature. The pressure of the air sample in the cold finger before expansion into the absorption cuvette amounts to 75–187 hPa corresponding to 2–5 cm^3 (STP) of air sample. After warming up, the cold finger is cooled down to −90°C to freeze out the remaining water vapor in the air sample. Finally, the cold finger is attached to an absorption cuvette of the spectrometer, and the air sample is expanded into the preevacuated absorption cuvette and analyzed within 9 min as described by *Güllük et al.* [1997].

The transfer procedure was tested by freezing out an air sample of known composition in the cold finger, transfering it into an absorption cuvette, and analyzing it as described above. No significant differences have been observed between the CO_2, CH_4, and N_2O concentrations and their nominal values.

2.4. Determination of the Trace Gas Concentration by the FM-TDLAS Spectrometer

Briefly, the FM spectra are measured for the CO_2, CH_4, and N_2O in the air sample. The air is then pumped out of the absorption cuvette, and the background FM spectra are taken with an empty cuvette. Finally, calibration gas with known CO_2, CH_4, and N_2O mixing ratios is filled at the sample pressure into the cuvette, and the calibration FM spectra are recorded. The CO_2, CH_4, and N_2O mixing ratios are then calculated from the amplitude ratios of sample and calibration FM spectra, both after the subtraction of the background spectrum.

Pressurized ambient air in a cylinder was used as a working standard. The CO_2, CH_4, and N_2O mixing ratios in the working standard gases were established using a primary standard certified by Climate Monitoring and Diagnosis Laboratory, National Oceanic and Atmospheric Administration (CMDL-NOAA). Mixing ratios of the target gases in the working standard air were (299.73 ± 0.20) ppm for CO_2, (1.717 ± 0.009) ppm for CH_4, and (295.8 ± 0.2) ppb for N_2O.

2.5. Blank Determination

The A and B vessels and the tubing connecting them to each other as well as to cold trap C are constructed symmetrically. The symmetrical construction of the apparatus allows one to reverse the functions of vessels A and B so that the ice sample having been sublimated into trap B can be sublimated back to vessel A by replacing the alcohol bath by the IR lamps and vice versa. This has the advantage that blank measurements (contamination released by the extraction procedure itself) can be performed by the sublimation of the original ice sample. In this way the time-consuming preparation of gas-free ice commonly used for this purpose is unnecessary. During "back sublimation" ~1–2 cm^3 (STP) of air with known composition is slowly introduced into the apparatus to simulate, as closely as possible, the sublimation of a natural ice sample containing air bubbles. The procedure blanks were then determined by comparison of the composition of the air added and the air exposed to the sublimation procedure.

2.6. Ice Samples

Simultaneous analysis of CO_2, CH_4, and N_2O was made of air samples extracted by sublimation from ice cores from Siple station (75°55'S, 83°55'W) in west Antarctica. The annual mean air temperature and snow accumulation rate at this drilling site are −24°C and 50 g cm^{-2} yr^{-1}, respectively. The drilling was made by a mechanical drill without fluid and was finished in November 1983 reaching a maximal depth of 200 m [*Neftel et al.*, 1985]. The ice at the bottom of the drilling is more than 300 years old. Air bubbles trapped in the ice are, however, younger. The mean difference between the age of the ice and the enclosed air is 82 years [*Schwander and Stauffer*, 1984].

The quality of the Siple ice core is excellent, and numerous measurements have been made of the mixing ratios of CO_2 [*Neftel et al.*, 1985; *Friedli et al.*, 1986] and CH_4 [*Stauffer et al.*, 1985] documenting the increases caused by increasing human activities during the past 200 years. So far, no N_2O measurements have been reported for this core. We analyzed nine ice samples (31–49 g) from different depths covering a time period of 200 years for CO_2, CH_4, and N_2O content. The oldest air sample dated back to 1772 A. D. and was taken at 176 m below surface, whereas the youngest sample dated from 1973 A. D. and was taken at 69 m below surface, just below the transition from firn to ice.

In addition to the Siple ice core a few samples were analyzed from two different drillings (3G and 4G2) at Vostok (78°28'S, 106°48'E, elevation 3490 m, annual mean temperature and snow accumulation rate of −55.5°C and 2.3 g cm^{-2} yr^{-1}, respectively [*Lorius et al.*, 1985]), the Russian station in central East Antarctica. The purpose of these measurements was mainly to investigate whether the sublimation extraction with almost 100% extraction efficiency will give air with the same mixing ratios as other extraction methods. Two samples from the 3G drilling were taken at 2043.7 m depth below surface. They have been dated to be between 151,000 and 155,000 years B. P. [*Lorius et al.*, 1985; *Barnola et al.*, 1987] corresponding to the end of the penultimate glacial period. Further samples were taken from 2306.1 m depth of the 4G2 drilling (maximum depth 2546 m). These air samples date back to ~181,500 years B. P., corresponding to the middle of the penultimate ice age.

3. Results and Discussion

Measurements presented here were made with the intention to verify the performance of the sublimation technique for the extraction of air samples from ice cores for simultaneous measurements of three greenhouse gases using FM-TDLAS spectroscopy. Consequently, samples were analyzed from the Siple

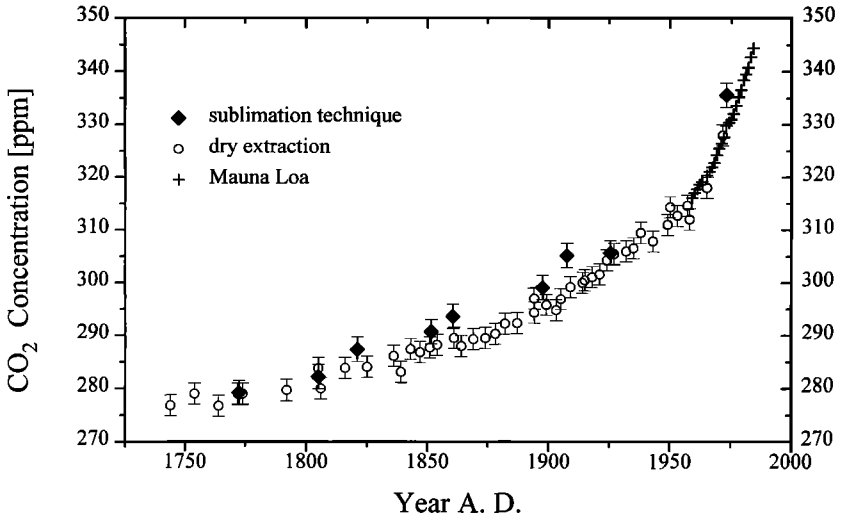

Figure 2. Temporal change of CO_2 mixing ratios between 1772 and 1973 as obtained from analyses of ice cores from Siple drilling (75°55'S, 83°55'W). Data measured by *Neftel et al.* [1985] and *Friedli et al.* [1986] on the same core using dry extraction technique are also shown as well as CO_2 data from direct atmospheric measurements at Mauna Loa reported by *Keeling et al.* [1989].

ice core, which had been thoroughly characterized in the past. To address the question of fractionation effects due to clathrate formation, several ice samples from deep parts of the Vostok ice cores were analyzed as well.

3.1. Tests of the Sublimation Procedure

The performance of the sublimation extraction procedure is characterized most appropriately by its blanks and their reproducibility. Blanks of the procedure were determined as described earlier. Averaged blanks from five determinations (average blank ± σ) were +11.0 ± 1.4 ppm for CO_2, +48.8 ± 5.8 ppb for CH_4, and +10.0 ± 1.1 ppb for N_2O in 5 cm^3 (STP) air. All blanks were positive; that is, the mixing ratios of CO_2, CH_4, and N_2O increase during the sublimation procedure. The blanks for CO_2, CH_4, and N_2O represent roughly 3% of their current atmospheric mixing ratios. The CO_2, CH_4, and N_2O mixing ratios reported below are corrected for these blanks.

Contamination of the air sample caused by the handling of the ice sample or by gases adsorbed at the ice surface during sample preparation is eliminated by the initial evacuation of the whole system and the sublimation of the outer layers of the ice sample. The leakage rate of the sublimation apparatus was determined from the pressure increase with the vacuum pump shut off and was found to be 2.24×10^{-6} hPa s^{-1}, corresponding to a volume of 0.0040 cm^3 (STP) of ambient air during a sublimation period of 30 min. Related to the typical air sample size of 2 cm^3 (STP), the contamination from leakage represents ~0.2%. In comparison with the experimentally determined blanks the contamination from leakage contributes to the blanks only to a small extent.

The strongest contamination source is apparently desorption from the systems walls and outgasing of the Viton-o-rings and Teflon-o-rings used to seal vessels A and B and the glass stopcocks. This experience is in agreement with that reported by *Zumbrunn et al.* [1982], who found that water vapor displaces CO_2 and possibly molecules of other gases from the apparatus walls. Blank runs of the apparatus without ice and without cooling down the cold traps but with the condensing of added air in the cold finger showed that a 2 cm^3 (STP) large dry air sample becomes depleted of CO_2 by 53–108 ppm (of initially 299.73 ppm) depending on the pretreatment of the apparatus. The highest depletion of 108 ppm was observed when the cold finger was heated during the evacuation period before injecting the air sample. This observation suggests that CO_2 is adsorbed on the walls of the apparatus. Regardless of the reasons for these artefacts, these observations clearly demonstrate that blank runs with a dry sublimation apparatus are not representative for wet conditions during the sublimation procedure. This conclusion led us to the blank determination procedure described above which simulates the conditions during the extraction as closely as possible and which leads to reproducible results for the blank value.

3.2. Measurements on Siple Ice Cores

Figures 2–4 show the results of the CO_2, CH_4, and N_2O measurements performed on the Siple core. The standard deviations $\pm\sigma$ of the measurements obtained from replicate extraction and analyses are ±2.0 ppm (n = 4) for CO_2, ± 8.5 ppb (n = 5) for CH_4, and ±1.7 ppb (n = 5) for N_2O. For comparison, measurements by other laboratories using different techniques for extraction and analysis of the air samples are also plotted in Figures 2–4. Figure 2 also shows the annual means of CO_2 mixing ratios measured at Mauna Loa [*Keeling et al.*, 1989]. Other CO_2 and CH_4 measurements on the Siple ice core in Figures 2 and 3, respectively, were originally reported by *Neftel et al.* [1985] and *Stauffer et al.* [1985]. CH_4 measurements in Figure 3 were later corrected by *Blunier* [1992] on the basis of six new measurements with improved milling technique [*Fuchs et al.*, 1991]. So far, no N_2O data have been reported for the Siple core. Consequently, Figure 4 shows N_2O data reported by *Machida et al.* [1995] for the Japanese ice core collected in 1991 at H15 (Antarctica, 69°05'S, 40°47'E, 1057 m above sea level, annual mean temperature and accumulation rate −20.5°C and 26 g cm^{-2} yr^{-1}, respectively) with a mechanical drill and with no fluid.

Figure 2 shows a good agreement of our CO_2 measurements obtained by the sublimation extraction procedure and FM-TDLAS analysis with data obtained by milling extraction and

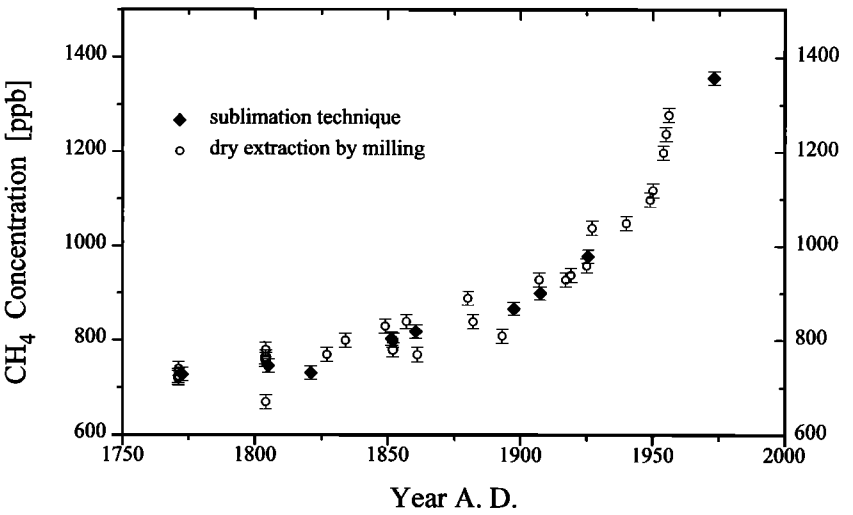

Figure 3. Temporal change of CH_4 mixing ratios between 1772 and 1973 as obtained from analyses of ice cores from Siple drilling (75°55'S, 83°55'W). Data determined by *Stauffer et al.* [1985] and *Blunier* [1992] on the same ice core using dry extraction by milling are also shown.

analysis by TDLAS analysis [*Neftel et al.*, 1985; *Blunier*, 1992]. Our measurements tend to be 4 ppm higher, but the number of measurements is too small to find any pattern in this tendency. The most probable reason for higher CO_2 values is that the apparatus blank used for correcting the CO_2 measurements is smaller than the actual one. However, the difference of 4 ppm is still within the combined uncertainty of our CO_2 blanks of ± 1.4 ppm, of our CO_2 measurements (extraction including analyses) of ± 2.0 ppm (both adding up to 2.4 ppm), and of the uncertainty of CO_2 measurements in Bern of 2 ppm [*Neftel et al.*, 1985; *Friedli et al.*, 1986]. The air sample dating from 1973 is just from below the transition zone where the permeability of very large ice samples, but not necessarily of small ones, is zero. This adds some uncertainty for the dating of air from this ice sample.

Figure 3 shows that our CH_4 measurements obtained by the sublimation extraction technique and analysis by FM-TDLAS spectroscopy are in excellent agreement with the earlier results determined using a milling device for extraction and gas chromatography for analysis [*Stauffer et al.*, 1985; *Blunier*, 1992]. Figure 4 shows also a very good agreement between our N_2O data and those reported by *Machida et al.* [1995] for Antarctica for the same period of time. Their data were obtained by milling 400–600 g ice [*Nakazawa et al.*, 1993a, b] and gas chromatographic analysis.

3.3. Measurements on Vostok Ice Cores

Our CO_2, CH_4, and N_2O measurements in ice samples from the 3G and 4G2 Vostok drillings are summarized in Table 1. It shows also CO_2 and CH_4 measurements made by Laboratoire de Glaciologie et Geophysique de L'Environment (LGGE) in Grenoble [*Barnola et al.*, 1987; *Jouzel et al.*, 1993] for comparison. They used crushing and melting techniques to extract air samples for CO_2 and CH_4 determination, respectively. Both gases were measured by gas chromatography.

Considering the combined uncertainty of our and LGGE's

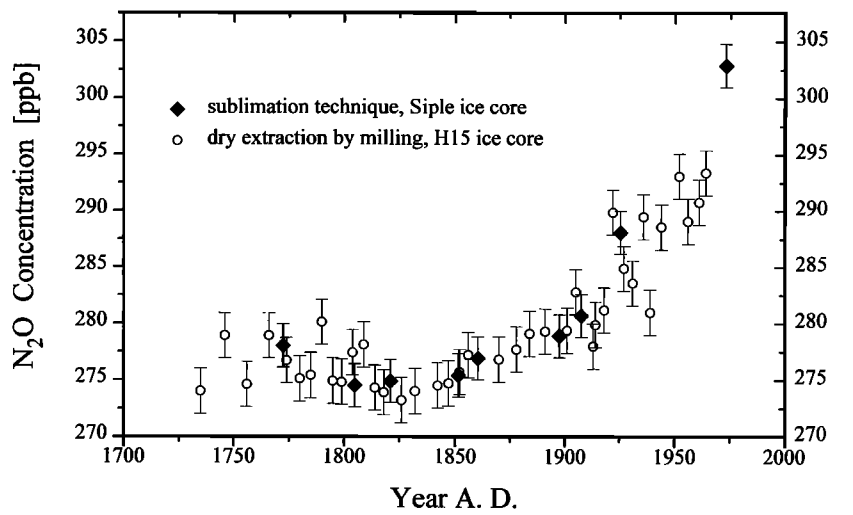

Figure 4. Temporal change of N_2O mixing ratios between 1772 and 1973 as obtained from analyses of ice cores from Siple drilling (75°55'S, 83°55'W). For comparison, N_2O data reported by *Machida et al.* [1995] on the H15 core from Antarctica are also shown.

Table 1. Results of the Measurements on Ice Cores 3G and 4G2 Drilled at Vostok Obtained by the Sublimation Technique (IFU)

Laboratory[a]	Depth, m	CO_2, ppm	CH_4, ppb	N_2O, ppb
		3G Drilling (Maximum Depth 2083 m)		
IFU	2043.7	187 ± 3 (n = 2)	370 ± 13	272 ± 3 (n = 2)
LGGE[b]	2050.3	191 ± 8		
LGGE[c]	2042.5		345 ± 23	
		4G2 Drilling (Maximum Depth 2546 m)		
IFU	2306.1	207 ± 3 (n = 6)	484 ± 36 (n = 3)	269 ± 4 (n = 5)
LGGE[d]	2302.1	199	456	

Data on the same cores but neighboring depths performed by LGGE using mechanical disintegration for CO_2 and melting for CH_4 are added for comparison.

[a]IFU, Fraunhofer-Institut fur Atmosphärische Umweltforschung; LGGE, Laboratoire de Glaciologie et Geophysique de L'Environment.

[b]*Barnola et al.* [1987].

[c]*Chappellaz et al.* [1990].

[d]*Jouzel et al.* [1993].

CO_2 and CH_4 measurements and the slightly different depths of the ice samples, our CO_2 and CH_4 data on the 3G core samples from 2043.7 m depth are in excellent agreement with measurements made at LGGE. The agreement of measurements on the 4G2 drilling is slightly worse but still within the analytical uncertainties of both laboratories and the additional uncertainty imposed by the age difference of the ice samples. So far, no N_2O data is available for comparison with our results at this depth.

4. Conclusions

The sublimation technique to extract air samples from ice cores combined with FM-TDLAS analysis provided synchronous CO_2, CH_4, and N_2O measurements on 20–50 g large ice samples. The amount of ice needed for measuring the three components is smaller than most laboratories need at present for the measurement of a single component [e.g., *Etheridge et al.*, 1988, 1992; *Machida et al.*, 1995]. The multicomponent air analysis in small ice samples can enable a more detailed investigation of the leads or lags in the changes of trace gas concentrations with the change of climate [e.g., *Raynaud et al.*, 1993].

Good agreement was observed between CO_2 measurements obtained by our sublimation extraction technique and measurements of other laboratories using the crushing techniques. The agreement of CO_2 measurements made by sublimation and crushing techniques on samples from Siple ice core dating back 200 years suggests that the content of CO_2 in the ice matrix, which would be inaccessible to crushing extraction techniques, is negligible. This observation is contrary to findings by *Wilson* [1995] but in line with the good agreement of measurements in ice with the direct measurements of CO_2 in air [*Neftel et al.*, 1995; *Etheridge et al.*, 1992; *Raynaud et al.*, 1993]. The major difference between our sublimation technique and that of *Wilson* [1995] is the collection of the extracted air sample. We freeze out the air sample at 14 K whereas *Wilson* [1995] isolates CO_2 from the air sample by first freezing out CO_2 in a cold trap at the temperature of liquid nitrogen and subsequently collecting the air sample on a molecular sieve kept at the temperature of liquid nitrogen. A further difference between the two methods is the determination of blank values. Wilson does not add any air in the sublimation vessel for his blank measurements. The good agreement of our CH_4 and N_2O measurements on Siple ice core with those made in Bern [*Blunier*, 1992] and Japan [*Machida et al.*, 1995] suggests that these gases are also not contained within the ice matrix to a significant degree.

The good agreement of our CO_2 and CH_4 measurements on Vostok ice cores with those made at LGGE in Grenoble suggests that the change in CO_2 and CH_4 concentration due to clathrate formation, if it occurs, is below the combined uncertainty of our and LGGE's measurements. *Jaworowski et al.* [1992, 1994] suggested that CO_2 measurements may be subject to fractionation due to clathrate formation and destruction. The good agreement of our CO_2 measurements with those made by LGGE using the milling extraction procedure makes this artefact unlikely.

The sublimation technique can also provide information about the influence of chemical reactions between impurities in the ice on the composition of the air bubbles. If CO_2 is produced by chemical reactions between impurities in the ice [*Anklin et al.*, 1995], the sublimation technique will be able to detect this CO_2 immediately after its production, while the crushing techniques detect it only after the CO_2 has entered the air bubbles. Therefore the new extraction technique will become an important tool for investigating the character and mechanisms of chemical reactions leading to a CO_2 surplus.

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